U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB80-119670

# Simultaneous Determination of Americium and Curium in Soil

(U.S.) Environmental Monitoring and Support Lab, Las Vegas, NV

14 Sep 78

## TECHNICAL REPORT DATA

*(Please read Instructions on the reverse before completing)*

| 1. REPORT NO. | 2. | 3. |
|---|---|---|
| EPA-600/J-79-039 | JOURNAL ARTICLE | PB80-119670 |

**4. TITLE AND SUBTITLE**
SIMULTANEOUS DETERMINATION OF AMERICIUM AND CURIUM IN SOIL

**5. REPORT DATE**

**6. PERFORMING ORGANIZATION CODE**

**7. AUTHOR(S)**
Michael H. Hiatt and Paul B. Hahn

**8. PERFORMING ORGANIZATION REPORT NO.**

**9. PERFORMING ORGANIZATION NAME AND ADDRESS**
Environmental Monitoring and Support Laboratory
U.S. Environmental Protection Agency
P. O. Box 15027
Las Vegas, NV 89114

**10. PROGRAM ELEMENT NO.**
INE 625

**11. CONTRACT/GRANT NO.**

**12. SPONSORING AGENCY NAME AND ADDRESS**
U.S. Environmental Protection Agency--Las Vegas, NV
Office of Research and Development
Environmental Monitoring and Support Laboratory
Las Vegas, Nevada 89114

**13. TYPE OF REPORT AND PERIOD COVERED**
Journal article

**14. SPONSORING AGENCY CODE**
EPA/600/07

**15. SUPPLEMENTARY NOTES**
Published in Analytical Chemistry, Febr. 1979, pp. 295-298
Contact: Michael H. Hiatt, 595-2969, ext. 385 (Las Vegas, NV)

**16. ABSTRACT**

A method is presented for the routine determination of americium and curium in 10 g of soil. The soil is dissolved with a mixture of nitric acid and hydrofluoric acid. Insoluble sulfates and phosphates are metathesized with boiling sodium hydroxide solutions. Plutonium and iron are sorbed on anion-exchange resin from 9 M hydrochloric acid after which the plutonium can be eluted and further purified for electrodeposition. Americium and curium are purified by cation-exchange and liquid-liquid chromatography. Mean recoveries of americium and curium were 58% and 56% respectively, for prepared soil samples. The minimum detectable activity for the individual nuclides is 0.002 pCi/g. For americium and curium activities of 0.1 to 1.0 pCi/g, the relative standard deviations for replicate analysis ranged from 3% to 8%. The deviations of the means from their known values were generally within ± 3%.

**17. KEY WORDS AND DOCUMENT ANALYSIS**

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| americium<br>curium<br>inorganic chemistry<br>plutonium<br>radiation pollution and control<br>soil | | 07B, E<br>68F |

| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS *(This Report)* | 21. NO. OF PAGES |
|---|---|---|
| RELEASE TO PUBLIC | UNCLASSIFIED | 6 |
| | 20. SECURITY CLASS *(This page)* | 22. PRICE |
| | UNCLASSIFIED | A02 - A01 |

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

REPRODUCED BY
NATIONAL TECHNICAL INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

ANALYTICAL CHEMISTRY, 51(2):295-298

EPA-600/J-79-039
JOURNAL ARTICLE

Published in ANALYTICAL CHEMISTRY, February 1979, pp. 295–298, by the American Chemical Society
Vol. 51, No. 2

# Simultaneous Determination of Americium and Curium in Soil

**Michael H. Hiatt* and Paul B. Hahn**

*U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, P.O. Box 15027, Las Vegas, Nevada 89114*

**A method is presented for the routine determination of americium and curium in 10 g of soil. The soil is dissolved with a mixture of nitric acid and hydrofluoric acid. Insoluble sulfates and phosphates are metathesized with boiling sodium hydroxide solutions. Plutonium and iron are sorbed on anion-exchange resin from 9 M hydrochloric acid after which the plutonium can be eluted and further purified for electrodeposition. Americium and curium are purified by cation-exchange and liquid–liquid chromatography. Mean recoveries of americium and curium were 58% and 56%, respectively, for prepared soil samples. The minimum detectable activity for the individual nuclides is 0.002 pCi/g. For americium and curium activities of 0.1 to 1.0 pCi/g, the relative standard deviations for replicate analysis ranged from 3% to 8%. The deviations of the means from their known values were generally within ±3%.**

The increasing demand to monitor $\alpha$-emitting nuclides near nuclear facilities has led to the development of different methodology for analysis of environmental soil samples (*1–8*). In this study it was desired to develop a method to determine americium and curium in 10-g soil samples which could be combined with existing methodology to determine plutonium. Although solvent extraction techniques have been extensively used for the isolation and purification of the actinide elements (*3, 5, 6*), this method employs ion-exchange techniques as this laboratory's experience has shown that far less manpower is required to routinely process large quantities of samples by column chromatography. An additional consideration was a reluctance to use large quantities of volatile organic solvents whose use may be deemed potentially hazardous.

The 10-g soil samples are dissolved with nitric and hydrofluoric acids (*8*). The sodium hydroxide metathesis and ammonium hydroxide precipitations render the sample soluble in strong hydrochloric acid where plutonium can then be isolated by anion-exchange chromatography (*7*).

Cation-exchange chromatography is used to separate the alkaline earths from the americium–curium fraction by using dilute hydrochloric acid eluents. Remaining trace contaminants are dramatically removed by using strong perchloric acid washes.

Americium-243 was used to trace both curium and americium in soil samples which were spiked with americium-241 and curium-243, -244. As fractionation between the americium-243 tracer and the curium spike was not observed, a curium nuclide is not necessary to trace in-situ curium when using this method. For environmental concentrations, interference from other transplutonium actinides is not considered to be a problem.

## EXPERIMENTAL

**Test Samples.** The soils analyzed were prepared by adding spikes of americium-241 and a mixture of curium nuclides, curium-243 and curium-244, to 10-g aliquots of standard plutonium soils. The nuclides added were previously calibrated by evaporation and $2\pi$ counting (*9*).

The standard soil samples contained plutonium in a refractory form and were also analyzed for plutonium to demonstrate that the dissolution procedure would solubilize and equilibrate refractory actinides with soluble tracer. The standard plutonium

soils were prepared by adding a known amount of plutonium-239 to 200-mesh soil, muffling at 700 °C for several hours, pulverizing, and blending with blank soil (*10*, *11*).

The analyses were traced with americium-243 and plutonium-236 tracers, also calibrated by evaporation and $2\pi$ counting.

**Soil Dissolution.** Add americium-243 tracer to 10 g of soil in a 250-mL TFE Teflon beaker. Add 60 mL 16 M nitric acid and 30 mL 29 M hydrofluoric acid and digest on a hot plate with occasional stirring for 1 h. Remove beaker from hot plate and add 30 mL each of 16 M nitric acid and 29 M hydrofluoric acid and continue digesting on a hot plate for 1 h. Remove the beaker from the hot plate and allow to cool. Cautiously add 20 mL of 12 M hydrochloric acid and continue digesting on a hot plate for 45 min. Add 5 g of boric acid and continue digesting for 15 min. Add 200 mg sodium bisulfate and evaporate the solution to an approximate volume of 10 mL (*8*). Neutralize the solution with the addition of 33% sodium hydroxide. Add 15 g of sodium hydroxide pellets, cover the Teflon beaker, and boil for 1 h to metathesize insoluble sulfates and phosphates. Cool the solution and transfer to a 500-mL pyrex centrifuge bottle and centrifuge. Discard the supernate and swirl the precipitate with 50 mL of distilled water and 1 g of boric acid. Acidify the slurry with 30 mL of 16 M nitric acid and allow to reflux on a hot plate for 0.5 h. Cool and adjust the pH to 9 with 14 M ammonium hydroxide. Centrifuge and again discard the supernate. Dissolve the resulting precipitate with 12 M hydrochloric acid and repeat both sodium and ammonium hydroxide precipitations using just enough 12 M hydrochloric acid to redissolve the precipitates (omit the addition of boric acid). Adjust the final solution to 6 M hydrochloric acid by adding an equal volume of 12 M hydrochloric acid and evaporating the solution to a volume of 40 to 50 mL. Cool and again add 12 M hydrochloric acid equal to the solution volume to adjust to 9 M in hydrochloric acid for the subsequent anion-exchange separation.

**Anion-Exchange Separation.** Pass the 9 M hydrochloric acid sample solution obtained from the dissolution through an anion-exchange column as described by Talvitie (*7*). Save the 9 M hydrochloric acid eluates (sample and three washes) for further americium and curium purifications. Talvitie's method can be continued for a plutonium determination.

**Cation-Exchange Separation.** Evaporate the 9 M hydrochloric acid eluates from the anion-exchange separation to 50 mL. Cool and transfer to a 250-mL centrifuge bottle. Adjust the pH to 9 with 14 M ammonium hydroxide. Centrifuge and discard the supernate. Dissolve the precipitate with 8 mL of 12 M hydrochloric acid, add 5 drops of 30% hydrogen peroxide and heat for 15 min. Allow to cool and dilute to a volume of 200 mL with distilled water.

Prepare a 1.4-cm i.d. column containing 24 mL of Bio-Rad 50W-X4, 50- to 100-mesh cation-exchange resin and condition with 100 mL of 0.5 M hydrochloric acid at a flow rate of 6 mL/min. Pass the 200-mL dilute hydrochloric acid sample through the column at a rate of 3 mL/min and discard the effluent. Rinse the centrifuge bottle with an additional 25 mL of 0.5 M hydrochloric acid, pass the rinse through the column, and discard the effluent. Elute alkaline earths and titanium with 200 mL of 1.0 M hydrochloric acid containing 2 drops 30% hydrogen peroxide and discard. Elute the americium and curium with 80 mL of 9 M hydrochloric acid and collect the eluate in a 100-mL beaker. Evaporate the solution to dryness, and dissolve the residue with 3 mL of 6 M hydrochloric acid; heat on a hot plate and allow to cool.

Prepare a 0.7-cm i.d. column containing 2.7 mL of Bio-Rad AG 50W-X4, 100- to 200-mesh resin in 0.5 M hydrochloric acid. Condition the column with 20 mL of 0.5 M hydrochloric acid. Dilute the americium and curium solution to 40 mL with distilled water and pass the solution through the freshly prepared cation ion-exchange column at the maximum flow rate. Discard the effluent. Rinse the beaker with consecutive 10- and 5-mL portions of 0.5 M hydrochloric acid and pass the rinses through the column. Discard the effluents. Elute any remaining iron with two successive 5-mL portions of 1.0 M ammonium thiocyanate followed by two successive 10-mL portions of 1.0 M hydrochloric acid. Remove the remaining non-rare earth impurities with successive 15- and 20-mL, 8.0 M perchloric acid washes. Elute americium, curium, and rare earth metals with one 10-mL and one 5-mL portion of 6 M hydrochloric acid and collect the effluents in a 50-mL beaker.

**Table I. Americium-241 Results**

| known activity,[a] pCi/g | | results,[b] pCi/g |
|---|---|---|
| 0.144 | | 0.134 ± 0.008 |
| | | 0.168 ± 0.008 |
| | | 0.156 ± 0.010 |
| | | 0.147 ± 0.008 |
| | | 0.143 ± 0.008 |
| | | 0.155 ± 0.010 |
| | | 0.144 ± 0.008 |
| | | 0.147 ± 0.008 |
| | | 0.127 ± 0.007 |
| | average | 0.147 ± 0.012[c] |
| 0.288 | | 0.292 ± 0.012 |
| | | 0.286 ± 0.012 |
| | | 0.277 ± 0.014 |
| | | 0.286 ± 0.012 |
| | | 0.308 ± 0.014 |
| | | 0.305 ± 0.014 |
| | average | 0.292 ± 0.012[c] |
| 0.576 | | 0.583 ± 0.019 |
| | | 0.609 ± 0.026 |
| | | 0.570 ± 0.020 |
| | average | 0.587 ± 0.020[c] |
| 0.720 | | 0.646 ± 0.021 |
| | | 0.678 ± 0.021 |
| | | 0.714 ± 0.026 |
| | average | 0.679 ± 0.034[c] |

[a] Prepared by spiking 10 g of blank soil with americium-241 calibrated by evaporation and $2\pi$ counting. [b] $1\sigma$ counting uncertainty. [c] Standard deviation of replicate determinations.

**Rare Earth Separation.** Remove the rare earths by the extraction chromatography method of Filer (*12*) using diethylenetriaminepentaacetic acid (DTPA) eluents with a column of bis(2-ethylhexyl)phosphoric acid (HDEHP) supported on Tee Six powder (Analabs, Inc., Hamden, Conn.). Add 20 mL 16 M nitric acid, 10 mL of 12 M perchloric acid and 1 mL of 18 M sulfuric acid to the DTPA eluents containing the americium and curium and evaporate the solution to sulfuric acid fumes and proceed with the electrodeposition.

**Electrodeposition.** Add 3 mL of distilled water to the fumed solution and heat gently on a hot plate. Transfer the solution to an electrodeposition cell and rinse the beaker with two 3-mL aliquots of 1:99 sulfuric acid. Adjust the resultant solution to the straw colored end point of thymol blue (pH 2–2.3) using ammonia vapors from an adapted wash bottle (inside stem removed) containing ammonium hydroxide. Electrodeposit at 1.1 A for 60 min (*13*).

## RESULTS AND DISCUSSION

Results of the analyses performed on 10-g soil samples containing known quantities of americium-241 and curium-243, -244 are presented in Tables I and II. The results of the multiple analyses agreed with the established values and no systematic errors were evident. Yields ranged from 42% to 67% for the americium-243 tracer. Relative standard deviations ranged from 3% to 8% for replicate americium and 4% to 7% for replicate curium determinations. Deviations of the means from the known values ranged from −6% to +2% for americium and −7% to −0.1% for curium. As there was no evidence of fractionation between americium and curium, americium-243 is a viable tracer for curium using this method for soils.

The equilibration of the soluble plutonium-236 tracer and the refractory plutonium-239 in the soils is shown by the

Table II. Curium-243 and Curium-244 Composite Results

| known activity,[a] pCi/g | results,[b] pCi/g |
|---|---|
| 0.219 | 0.192 ± 0.010 |
| | 0.231 ± 0.010 |
| | 0.232 ± 0.012 |
| | 0.219 ± 0.011 |
| | 0.216 ± 0.010 |
| | 0.207 ± 0.010 |
| | average 0.216 ± 0.013[c] |
| 0.438 | 0.387 ± 0.017 |
| | 0.389 ± 0.018 |
| | 0.395 ± 0.016 |
| | 0.409 ± 0.015 |
| | 0.432 ± 0.018 |
| | 0.427 ± 0.018 |
| | average 0.406 ± 0.019[c] |
| 1.09 | 1.035 ± 0.030 |
| | 1.156 ± 0.043 |
| | 1.076 ± 0.033 |
| | average 1.089 ± 0.062[c] |

[a] Prepared by spiking 10 g of blank soil with a mixture of $^{243}Cm$ + $^{244}Cm$ calibrated by evaporation and $2\pi$ counting. [b] $1\sigma$ counting uncertainty. [c] Standard deviation of replicate determinations.

Table III. Refractory Plutonium-239 Results

| | known activity, pCi/g | results[a] | runs |
|---|---|---|---|
| $^{239}Pu$ | 0.0509 | 0.0489 ± 0.0046 | 6 |
| $^{239}Pu$ | 0.464 | 0.445 ± 0.031 | 9 |
| $^{239}Pu$ | 2.60 | 2.50 ± 0.16 | 6 |

[a] Standard deviation of replicate determination.

determinations of plutonium-239 reported in Table III. These results demonstrate the solubility of the refractory actinides using the nitric acid and hydrofluoric acid soil dissolution.

Ten grams of soil has been chosen as an adequate sample size for the desired sensitivity and to minimize discrepancies due to the particulate nature of actinides in some soils (*10*, *14*). The hydrofluoric acid–nitric acid dissolution of 10 g of soil results in a cumbersome salt burden. An actinide-concentrating precipitation, such as ferric hydroxide, is necessary to remove salts enabling ion-exchange chromatography in a moderate size column.

The hydroxide precipitations were found to be necessary to aid the dissolution of insoluble actinides and to remove large quantities of interfering cations and salts. Additional investigation showed that without use of the sodium hydroxide precipitations, americium-241 (0.06 MeV $\gamma$) was found in undissolved residues from the original dissolution by Ge(Li) counting. Further analysis of such residues by X-ray diffraction detected sulfur at significant levels suggesting the presence of insoluble sulfates which would carry the actinides. The addition of the sodium hydroxide metathesis step resulted in the complete dissolution of americium prior to the anion-exchange separation.

The ammonium hydroxide precipitations are necessary to remove significant portions of calcium generally found in soil samples. If significant quantities remain, calcium may precipitate as a chloride in the 9 M hydrochloric acid solution and inhibit the anion-exchange separation. In 10-g soil samples, the concentration of alkaline earths still remaining after the ammonium hydroxide precipitations is still great enough that cation-exchange separations are necessary to eliminate alkaline earth contamination in the final americium–curium electrodeposition. The alkaline earth removal is accomplished by the 1.0 M hydrochloric acid washes in the cation-exchange separations (*15*).

The efficiency of the hydroxide precipitations for concentrating americium and other actinides of interest was determined by spiking 10 g of background soil, dissolving the soil as described, and analyzing the decanted supernates from the various precipitations. Values reported in Table IV are percentages lost to the supernates. Initial spikes were approximately 10 nCi. Attempts were not made to prevent absorption of carbon dioxide in the sodium hydroxide solutions and absorbed carbonate anions could account for the high uranium losses observed. The losses for the other nuclides were found to be minimal.

Sorption characteristics of the elements on cation-exchange resin in perchloric acid (*15*) suggested the use of 8 M perchloric acid washes to remove any remaining interferences since only a few elements besides the rare earths and actinides are sorbed from such a solution. The use of these washes was found to increase recoveries and dramatically increase $\alpha$ spectral resolution.

The concentrations of rare earths encountered in 10-g soil samples can also cause spectral resolution to diminish. In previous analyses, the rare earth concentrations were so great in many samples as to deposit a 1-mm thick layer of rare earth oxides on the planchet. For this reason, the removal of rare earths by liquid–liquid extraction chromatography using HDEHP-treated Teflon columns is considered necessary for soils (*12*).

Preliminary evidence has demonstrated that the method may be useful for the analysis of other types of environmental samples. Biological samples can be prepared for this method by ashing, dissolution in hydrofluoric acid–nitric acid, and precipitating the actinides with ammonium hydroxide. The sample can then be dissolved in 9 M hydrochloric acid and processed by continuing with the anion-exchange separation. Water samples can be analyzed by this method with an initial ammonium hydroxide coprecipitation utilizing an iron carrier. When the volume of the precipitate is large, the sample can be treated like the 10-g soil sample. When the amount of precipitate is small, the hydrofluoric acid–nitric acid dissolution can be abbreviated and subsequent hydroxide precipitations eliminated. Glass fiber air filter samples can be treated identically to the soils without appreciable differences in the yields. Non-soil samples do not require the rare earth separation.

Table IV. Analysis of Hydroxide Supernates

| | sodium hydroxide supernates, % | | | ammonium hydroxide supernates, % | | | combined supernates, % |
|---|---|---|---|---|---|---|---|
| | 1st | 2nd | total | 1st | 2nd | total | |
| $^{208}Po$ | 0.4 | 1.0 | 1.4 | 0.5 | 0.9 | 1.4 | 2.8 |
| $^{238}Pu$ | 0.4 | 0.2 | 0.3 | 0.0 | 0.0 | 0.0 | 0.3 |
| $^{243}Am$ | 0.1 | 0.2 | 0.3 | 0.1 | 0.1 | 0.2 | 0.5 |
| $^{230}Th$ | 0.5 | 0.3 | 0.8 | 0.0 | 0.0 | 0.0 | 0.8 |
| $^{237}Np$ | 0.1 | 0.4 | .05 | 0.8 | 0.3 | 1.1 | 1.6 |
| $^{238}U$ | 8.3 | 27.3 | 35.6 | 0.1 | 0.2 | 0.3 | 35.9 |

The minimum detectable activity for an $\alpha$ peak region with a 0.003 cpm background and a detector with 22% counting efficiency is 0.01 pCi for a 1000-min counting time. A 10-g sample with a 50% chemical yield would then give a 0.002 pCi/g minimum detectable limit for an americium or curium determination.

## LITERATURE CITED


(1) R. Bojanowski, H. D. Livingston, D. L. Scheider, and D. R. Mann, "A Procedure for the Analysis of Americium in Marine Environmental Samples", Reference Methods for Marine Radioactivity Studies II, International Atomic Energy Agency, Vienna, Technical Report Series No. 169 (1973).
(2) M. C. de Bortoli, *Anal. Chem.*, **39**, 375 (1967).
(3) B. L. Hampson and D. Tennant, *Analyst (London)*, **98**, 873 (1973).
(4) S. A. Reynolds and T. G. Scott, *Radiochem. Radioanal. Lett.*, **23** (4), 269 (1975).
(5) T. G. Scott and S. A. Reynolds, *Radiochem. Radioanal. Lett.*, **23** (4), 275 (1975).
(6) C. W. Sill, K. W. Puphal, and F. D. Hindman, *Anal. Chem.*, **46**, 1725 (1974).
(7) N. A. Talvitie, *Anal. Chem.*, **43**, 1827 (1971).
(8) U.S. Atomic Energy Commission, "Measurement of Radionuclides in the Environment—Sampling and Analysis of Plutonium in Soil", U.S. AEC Regulatory Guide 4.5 (1974).
(9) C. W. Sill, *Anal. Chem.* **46**, 1426 (1974).
(10) P. B. Hahn, E. W. Bretthauer, P. B. Altringer, and N. F. Mathews, "Fusion Method for the Measurement of Plutonium in Soil: Single-Laboratory Evaluation and Interlaboratory Collaborative Test", Office of Research and Development, U.S. Environmental Protection Agency, EPA-600/7-77-078 (1977).
(11) C. W. Sill and R. D. Hindman, *Anal. Chem.*, **46**, 113 (1974).
(12) T. D. Filer, *Anal. Chem.*, **46**, 608 (1974).
(13) N. A. Talvitie, *Anal. Chem.* **44**, 280 (1972).
(14) C. W. Sill, *Health Phys.*, **29**, 619 (1975).
(15) F. Nelson, T. Murase, and K. A. Krause, *J. Chromatogr.*, **13**, 503 (1964).


RECEIVED for review September 14, 1978. Accepted November 21, 1978.